PATENT SPECIFICATION

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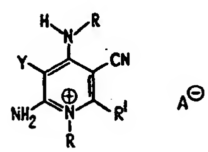
(19)

(54) PYRIDINIUM SALTS

(71) We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION, a Body Corporate established under the Science and Industry Research Act 1949—1968, carrying on scientific and industrial research, of Limestone Avenue, Campbell in the Australian Capital Territory, Commonwealth of Australia, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel pyridinium salts which exhibit useful fungicidal properties, to methods for the preparation of these salts, and to methods and compositions for controlling the growth of fungi.

In particular, the present invention relates to novel pyridinium salts of the general formula I;



(I)

wherein

Y is hydrogen or halogen, especially chlorine or bromine;

R is straight- or branched-chain, substituted or unsubstituted alkyl or allyl, especially an alkyl group of one to twelve carbon atoms and more particularly an alkyl group of five to ten carbon atoms; substituted or unsubstituted cycloalkyl, especially a cycloalkyl group of five to ten carbon atoms; or aralkyl especially a benzyl or phenylethyl group;

R′ is hydrogen, halogen, especially a chlorine or bromine atom; sulphonate; azido; a radical of the formula —NH—SO_2—R_1, wherein R_1 represents a substituted or unsubstituted aryl group or a straight or branched-chain, substituted or unsubstituted alkyl group; a radical of the formula

$$—S—\underset{\underset{\displaystyle S}{\|}}{C}—N(\text{lower alkyl})_2;$$

a radical of the formula —CH(CN)—R_2 wherein R_2 represents —COOH, —COO— —(lower alkyl) or —NH—CO—NH_2; or a radical of the formula

—NH—R″,
—S—R″ or
—O—R″

wherein

R″ represents hydrogen, substituted or unsubstituted, straight- or branch-

chain alkyl, alkenyl or alkynyl, substituted or unsubstituted aryl or aralkyl, or cyano;

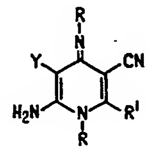
and

A⊖ which is not present when R′ contains an anionic group, represents a halide anion, especially a chloride or bromide ion. By "lower alkyl" is meant alkyl of 1 to 8 carbon atoms.

Typical substituents which may be introduced in the alkyl, alkenyl, alkynyl, cycloalkyl, aryl or aralkyl groups include halo radicals, particularly chloro or bromo radicals, and nitro, lower-alkoxy, pyridyl, carboxyl or furyl radicals.

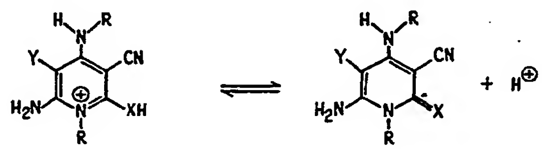
It will be apparent that when in the above general formula R′ represents a sulphonate radical ($-SO_3^{\ominus}$) or another radical containing an anionic group, the anion A⊖ will not be present.

It will be apparent to persons skilled in this art that by removal of a proton from the compounds of general formula I, an imine conjugate base Ia will be formed.



Ia

It will also be apparent that where R′ represents a radical of the formula —XH in which X represents —S— or —O—, removal of a proton will also form a base Ib as set out below.

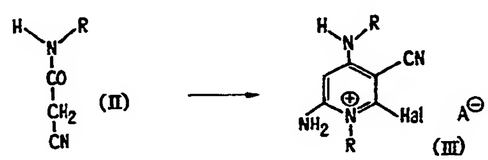


Ib

Since these compounds may be used either in the form of a salt or in the form of the base, reference herein to compounds of the general formula I are to be understood as references to those compounds either as a salt or as the base.

As typical compounds of the general formula I, there may be mentioned those in which Y represents a hydrogen atom, R′ represents a chlorine atom and R represents n- or iso-butyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl or n-nonyl, and those in which Y represents a bromine atom, R′ represents a chlorine atom and R represents n-hexyl or n-octyl. Other typical compounds are set out in the Examples below.

The compounds of this invention in which Y represents a hydrogen atom, R′ represents a halogen atom and R is a defined above may be prepared by the reaction of an N-substituted cyanoacetamide of the formula II with a phosphorous halide or oxyhalide under known reaction conditions to form a compound of formula III:



In a typical procedure, the N-substituted cyanoacetamide is dissolved in an organic solvent such as chloroform and phosphorous oxychloride added to the solution. The reaction mixture is then warmed on a steam bath under reflux for about two hours and the product collected and recrystallised.

The compounds of the formula III may then be halogenated in the 3-position and/or the 6-halo substituent is replaced by other radicals represented by R′ as hereinbefore defined in manner known *per se* to form other compounds of the general formula I. By "manner known *per se*" is meant a manner heretofore used

or described in the chemical literature. Typical procedures are illustrated in the Examples below.

It has been found that the compounds of this invention show a range of anti-fungal activity and the typical compounds mentioned above have been found to completely inhibit spore germination in *Monolinia fructicola* at 1—100 ppm, to control *Phytophthora cinnamomi* infection of lupin seedlings at 1—8 ppm and to prevent infection of tomato seedlings by *Fusarium oxysporum* and cotton seedlings by *Rhizoctonia solani* when incorporated in the soil at 8 kg/ha.

In another aspect, this invention therefore provides a method of controlling fungal infection of plants which comprises treating the fungi, the plants, the soil or the plant seed with an effective amount of a compound of formula I.

The amount of the compound of general formula I necessary to achieve the desired control in carrying out the above methods may be readily determined by simple experimentation and, by way of example, amounts of particular compounds within this general formula which may be used to control growth of fungi have been mentioned above.

In accordance with a further aspect of this invention there are provided compositions for controlling the growth of fungi which comprise an inert carrier and an effective amount of a compound of the general formula I. The compositions according to this aspect may be either liquid or solid as desired. The precise formulation employed may be varied according to the manner in which it is to be applied, the extent of control desired or necessary and the particular type of fungi to be controlled. The most advantageous composition for the control of a specific fungi may be readily determined by persons of ordinary skill in the art by routine experimentations in accordance with the teaching of this invention and the various factors set out above.

The compositions may be formulated with solid inert carriers, such as finely divided talc or silica to give powder compositions or vermiculites to give granular compositions. Alternatively, liquid inert carriers may be used, such as vegetable or mineral oils, to provide spray compositions. In addition to the compound of general formula Ia and inert carrier, the compositions according to this invention may include other active components to assist the formulation and use of the compositions, such as emulsifying, dispersing and wetting agents.

One example of the manner in which the compounds of the present invention may be used is by formulation into a composition for spraying cotton plants prior to harvesting. A compound of the present invention is incorporated into a known spray composition which also includes a defoliating agent and the composition containing both active agents is sprayed onto the cotton plants to provide fungicidal protection at the same time as the plants are defoliated.

The following Examples illustrate the present invention.

EXAMPLE 1.

N-methyl cyanoacetamide (9.8 g, 0.1 mole) was dissolved in chloroform (50 ml) and phosphorous oxychloride (15.3 g., 0.1 mole) added. The reaction mixture was warmed on a steam bath under reflux for 2 hours during which time the product, 2-amino-6-chloro-5-cyano-1-methyl-4-methylamino pyridunium choride (compound 1—table 1) crystallized. It was collected and recrystallized from methanol to give a pale yellow solid (9.4 g., 80%) [m.p. 250°C, C 41.51 (41.21); H 4.26 (4.32); N 24.11 (24.03); Cl 30.3 (30.4)]

Higher homologues in the series were soluble in chloroform and were isolated by removal of the solvent in vacuo and treatment of the residue with cold methanol.

Other compounds of formula III, in which Hal represents chlorine and R is as set out in Table 1 below, were prepared in a similar manner.

Examples 2 to 6 illustrate halogenation of compounds of formula III in the 3-position and substitution in the 6-position.

EXAMPLE 2.

3.37 gms (.01 mole) of 2-amino-6-chloro-5-cyano-1-n-hexyl-4-*n*-hexylamino pyridinium chloride (compound II—Table 1) was dissolved in methanol and 1.0 gm (.01 mole) of triethylamine and 0.8 g. (.011 mole) of n-butylamine added. The solution was refluxed for 1 hour and on cooling 2.5 g (60% yield) of 2-amino-6-*n*-butylamino-5-cyano-1-n-hexyl-4-*n*-hexylamino pyridinium chloride (compound 42—Table 2) crystallised out. [m.p. 179—180°C. C 64.88 (64.6) H 9.81 (9.78) N17.11 (17.1)].

Other derivatives prepared in a similar manner using different pyridinium salts and a variety of amines and amides are listed in Table 2.

EXAMPLE 3.

3.2 g (0.1 mole) of 2-amino-1-n-butyl-4-n-butylamino-6-chloro-5-cyano-pyridinium chloride (compound 6—Table 1) was dissolved in hot water and 1.5 g (.012 moles) of sodium sulphite added. One cooling 2.8 g (85% yield) of 2-amino-1-n-butyl-4-n-butylamino-5-cyano-pyridinium betaine-6-sulphonate (compound 60—Table 3) crystallised out and was filtered off. [MPt 240—245°C with decomposition. C 51.31 (51.51) H 6.76 (6.79) N 16.70 (17.17) S 9.9 (9.8)].

Other derivatives prepared in a similar manner (aqueous alcohol could be used in the case of less water soluble starting materials) are listed in Table 3.

EXAMPLE 4.

4.85 g (.01 mole) of 2-amino-6-chloro-5-cyano-1-n-decyl-4-n-decylamino pyridinium chloride (compound 16—Table 1) was suspended in water and 1.8 g (.012 mole) bromine added to the rapidly stirred suspension which was heated on a water bath for 30 minutes. On cooling 4.5 g (75% yield) of 2-amino-3-bromo-6-chloro-5-cyano-1-n-decyl-4-n-decylamino pyridinium bromide (compound 70 Table 4) was filtered off and recrystallised from ethanol. [MPt 166—168°C. C 51.62 (51.27) H 7.31 (7.40) N 9.20 (9.20)].

Other derivatives prepared similarly are listed in Table 4.

EXAMPLE 5.

(a) 2.3 g (.01 mole) of 2-amino-6-chloro-5-cyano-1-methyl-4-methylamino pyridinium chloride (compound 1—Table 1) was dissolved in water and 0.92 g (.01 mole) of thioglycollic acid and 2.0 g (.02 mole) of triethylamine added. After 30 minutes of 1.5 g (60% yield) of 2-amino-5-cyano-1-methyl-4-methylamino-pyridinium-betaine-6-thioglycollate (compound 74—Table 5) was filtered off (MPt>240°C).

(b) 3.15 g (.01 mole) of 2-amino-1-n-butyl-4-n-butylamino-6-chloro-5-cyano pyridinium chloride (compound 6 Table 1), 1.24 g (.01 mole) of benzyl mercaptan and 1.0 g (.01 mole) of triethylamine were dissolved in dimethylformamide and heated at 100°C for 1 hour. The dimethylformamide was evaporated off, ethanol added and 2.0 g (50% yield) of 2-amino-6-benzylmercapto-1-n-butyl-4-n-butyl-amino-5-cyano pyridinium chloride (compound 75—Table 5) crystallised out and was recrystallised from ethanol (MPt 145—147°C).

(c) 4.5 g (.01 mole) of 2-amino-6-chloro-5-cyano-1-n-octyl-4-n-octylamino pyridinium chloride (compound 14—Table 1) was dissolved in dimethylformamide and 2.2 g (.01 mole) of sodium diethyldithiocarbamate added and the solution refluxed for 60 minutes. This was then cooled, filtered and the solvent evaporated off. Methanol was added and 1.6 g (30% yield) of 2-amino-5-cyano-6 - diethylthio - carbamylthio - 1 - n - octyl - 4 - n-octylamino pyridinium chloride (compound 80—Table 5) was filtered off and recrystallised from methanol (MPt 124—126°C.)

(d) 3.7 g (.01 ml) of 2-amino-6-chloro-5-cyano-1-n-hexyl-4-n-hexylamino pyridinium chloride (compound 11—Table 1) was dissolved in ethanol and 1.1 g (.01 mole) thiophenol and 1.0 g (.01 mole) of triethylamine added. The solution was left 16 hours at room temperature poured into iced water and 2.3 g (50% yield) of 2-amino-5-cyano-1-n-hexyl-4-n-hexylamino-6-phenylmercapto pyridinium chloride (compound 78—Table 5) filtered off (MPt 227—228°C).

Analogous compounds prepared by similar methods to those described in examples 5(a) (b) (c) and (d) are listed in Table 5.

EXAMPLE 6.

(a) 3.2 g (.01 mole) of 2-amino-1-n-butyl-4-n-butylamino-6-chloro-5-cyano-pyridinium chloride (compound 6—Table 1) was dissolved in hot water, 4.0 g (.04 mole) of triethylamine added and the solution refluxed on a boiling water bath. After 2 hours 2.0 g (75% yield) of 2-amino-1-n-butyl-4-n-butylamino-5-cyano-pyridine-6-one (compound 87—Table 6) had precipated and was filtered off. (MPt 177—179°C).

(b) 2.6 g (.01 mole) of 2-amino-6-chloro-5-cyano-10-ethyl-4-ethylamino pyridinium chloride (compound 2—Table 1) was dissolved in water and (.03 mole) of sodium sulphide added. 2.0 g (90% yield) of 2-amino-5-cyano-1-ethyl-4-

ethylamino pyridine-6-thione (compound 85—Table 6) immediately precipitated and was filtered off. (MPt 190—192°C).

(c) 2.3 g (.01 mole) of 2-amino-6-chloro-5-cyano-1-methyl-4-methylamino pyridinium chloride (compound 1—Table 1) was dissolved in water and 0.66 g (.01 mole) of malononitrile and 2.0 g (.02 mole of triethylamine added. After a few minutes 1.7 g (75% yield) of 2-amino-5-cyano-1-methyl-4-methylamino-6-dicyanomethyl pyridinium chloride (compound 83—Table 6) (MPt>240°C) crystallised out.

A number of analogous conjugate bases prepared according to the method described in (a) (b) and (c) above are listed in Table 6.

EXAMPLE 7.

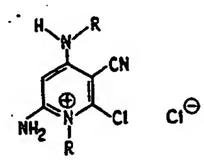
0.8 g (.012 mole) of sodium azide was added to an aqueous solution containing 2.6 g (.01 mole) of 2-amino-6-chloro-5-cyano-1-ethyl-4-ethylamino pyridinium chloride (compound 2—Table 1) left for 2 hours at room temperature and then cooled. 2.0 g (70% yield) of 2-amino-6-azido-5-cyano-1-ethyl-4-ethylamino pyridinium chloride crystallised out (MPt 164—165°C).

EXAMPLE 8.

3.2 g (.01 mole) of 2-amino-1-n-butyl-4-n-butylamino-6-chloro-5-cyano-pyridinium chloride (compound 6—Table 1) was dissolved in dry dimethyl formamide, .06 g (.01 mole) of sodium methoxide added, and the mixture refluxed for 60 minutes, filtered and solvent evaporated off. The solid was recrystallised from acetone to give 1.0 g (30% yield) of 2-amino-1-n-butyl-4-n-butylamino-5-cyano-6-methoxy pyridinium chloride (MPt 187—189°C).

TABLE 1.

Compounds of the formula:



prepared as in Example 1.

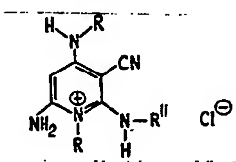
Product Compound No.	R	% Yield	MPt(°C)	ANALYSIS C	H	N	Cl
1	Methyl	80	250	41.51 (41.21)	4.26 (4.32)	24.11 (24.03)	30.3 (30.4)
2	ethyl	80	>250				
3	n-propyl	75	215—217				
4	isopropyl	40	196—197	49.89 (49.81)	6.51 (6.27)	19.25 (19.37)	
5	alkyl	60	192—194				
6	n-butyl	85	230—231	52.88 (53.16)	6.94 (7.01)	17.99 (17.71)	22.7 (22.4)
7	isobutyl	50	237—239				
8	sec-butyl	30	177—178	52.73 (53.16)	7.06 (7.01)	17.61 (17.71)	
9	n-pentyl	80	238—240				

TABLE 1 (continued).

Product Compound No.	R	% Yield	MPt(°C)	ANALYSIS C	H	N	Cl
10	cyclopentyl	70	205—207	56.44 (56.29)	6.46 (6.49)	16.40 (16.41)	21.0 (20.8)
11	n-hexyl	75	202—204	58.21 (57.90)	7.80 (8.04)	15.16 (15.00)	18.8 (19.0)
12	cyclohexyl	60	213—214	58.51 (58.53)	6.97 (7.10)	15.26 (15.17)	18.8 (19.2)
13	n-heptyl	80	238—240				
14	n-octyl	75	233—234	61.85 (61.52)	8.93 (8.91)	13.07 (13.04)	16.4 (16.5)
15	n-nonyl	75	230—232	63.2 (63.3)	9.19 (9.20)	12.25 (12.40)	15.5 (15.3)
16	n-decyl	75	226—228	64.3 (64.7)	9.48 (9.69)	11.54 (11.78)	14.6 (14.3)
17	benzyl	50	192—194	62.09 (62.34)	5.01 (4.67)	14.79 (14.55)	18.1 (18.4)
18	phenylethyl	50	>240				

TABLE 2.

Compounds of the formula:



prepared as in Example 2.

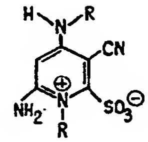
Starting Compound No.	Reactant	R	R″	Product Compound No.	% Yield	MPt(°C)
1	ammonia	methyl	H	19	70	>240
1	cyanamide	methyl	cyano	20	20	>240
1	N-propylamine	methyl	n-propyl	21	80	>240
1	allylamine	methyl	allyl	22	70	>240
1	furfurylamine	methyl	furfuryl	23	60	>240
1	benzylamine	methyl	benzyl	24	80	>240
1	p-toluenesul-phonamide	methyl	p-toluene-sulphonyl	25	90	>240
1	n-octylamine	methyl	n-octyl	26	60	203—205
1	n-dodecyl-amine	methyl	n-dodecyl	27	80	210—214

TABLE 2 (continued).

Starting Compound No	Reactant	R	R″	Product Compound No	% Yield	MPt(°C)
1	glycine	methyl	carboxymethyl	28	80	>240
2	2-bromoethyl-amine	ethyl	2-bromoethyl	29	80	>240
2	furfurylamine	ethyl	furfuryl	30	80	>240
2	2-picolylamine	ethyl	-picolyl	31	75	233—234
3	furfurylamine	n-propyl	furfuryl	32	75	225
4	n-butylamine	isopropyl	n-butyl	33	85	188—190
4	furfurylamine	isopropyl	furfuryl	34	85	202
6	n-butylamine	n-butyl	n-butyl	35	80	224
6	furfurylamine	n-butyl	furfuryl	36	80	248
6	n-octylamine	n-butyl	n-octyl	37	60	228—229
6	glycine	n-butyl	carboxymethyl	38	80	>240
10	cyanamide	cyclopentyl	cyano	39	70	>240
11	methylamine	n-hexyl	methyl	40	30	228—230
11	furfurylamine	n-hexyl	furfuryl	41	50	>240
11	n-butylamine	n-hexyl	n-butyl	42	60	179—180
11	n-hexylamine	n-hexyl	n-hexyl	43	70	159—160
11	n-octylamine	n-hexyl	n-octyl	44	50	148—151
12	methylamine	cyclohexyl	methyl	45	60	205—207
14	ammonia	n-octyl	H	46	90	231—233
14	methylamine	n-octyl	methyl	47	80	156
14	cyanamide	n-octyl	cyano	48	90	226
14	ethylamine	n-octyl	ethyl	49	80	209—211
14	n-propylamine	n-octyl	n-propyl	50	80	170—172
14	n-butylamine	n-octyl	n-butyl	51	80	158—160
14	furfurylamine	n-octyl	furfuryl	52	50	192—194
14	n-hexylamine	n-octyl	n-hexyl	53	60	140—142
14	n-octylamine	n-octyl	n-octyl	54	50	154—156
16	ammonia	n-decyl	H	55	60	>240
17	cyanamide	benzyl	cyano	56	80	>240

TABLE 3.

Compounds of the formula:

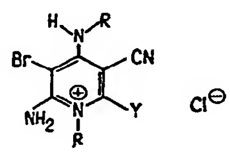


prepared as in Example 3.

Starting Compound No.	R	Product Compound No	% Yield	MPt(°C)	ANALYSIS C	H	N	S
1	methyl	57	85	>240	39.27 (39.67)	4.26 (4.16)	22.76 (23.13)	13.0 (13.2)
2	ethyl	58	80	>240				
4	isopropyl	59	80	>240				
6	n-butyl	60	85	240—245	51.31 (51.51)	6.76 (6.79)	16.70 (17.17)	9.9 (9.8)
7	isobutyl	61	90	>240				
12	cyclohexyl	61	60	>240	56.95 (57.12)	6.85 (6.92)	14.61 (14.80)	8.2 (8.5)
14	n-octyl	63	80	240—241				

TABLE 4.

Compounds of the formula:

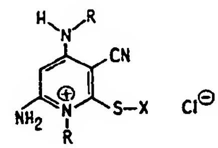


prepared as in Example 4.

Starting Compound No.	R	Y	Product Compound No.	% Yield	MPt(°C)
3	n-propyl	chloro	64	80	125—128
59	iso-propyl	sulphonate	65	60	>240
6	n-butyl	chloro	66	60	178—180
11	n-hexyl	chloro	67	50	182—184
14	n-octyl	chloro	68	90	166—167
15	n-nonyl	chloro	69	70	169—171
16	n-decyl	chloro	70	75	166—168
17	benzyl	chloro	71	70	136—138
56	benzyl	cyanamino	72	80	>240

TABLE 5.

Compounds of the formula



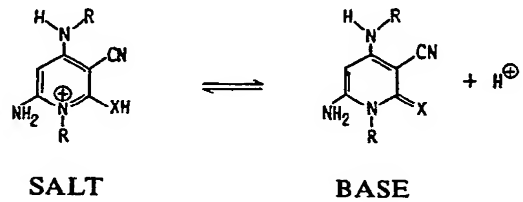
prepared as in Example 5.

Starting Compound No	R	X	Product Compound No	% Yield	MPt(°C)
1	methyl	benzyl	73	40	145—147
1	methyl	$—CH_2COO^{\ominus}$	74*	80	>240
6	n-butyl	benzyl	75	50	145—147
6	n-butyl	$—CH_2COO^{\ominus}$	76*	50	>240
6	n-butyl	dimethylthio-carbamoyl	77	70	169—171
11	n-hexyl	phenyl	78	50	227—228
12	cyclohexyl	phenyl	79	50	227—229
14	n-octyl	diethylthio-carbamoyl	80	30	124—126

*In these two compounds the chloride ion is absent.

TABLE 6.

Compounds of the formula



prepared as in Example 6.

Starting Compound No	R	XH	Product Compound No	% Yield	MPt (°C) (Base form)
1	methyl	hydroxy	81	80	>240
1	methyl	mercapto	82	80	>240
1	methyl	dicyano-methyl	83	75	>240
1	methyl	carboethoxy-cyanomethyl	84	60	>240
2	ethyl	mercapto	85	90	190—192
2	ethyl	carbamido-cyanomethyl	86	70	227—228
6	n-butyl	hydroxy	87	75	177—179
6	n-butyl	mercapto	88	80	173—175
1	n-hexyl	mercapto	89	70	103—104

The anti-fungal activity of typical compounds according to the present invention is illustrated in the results set out in Table 7 below.

TABLE 7.

Compound No	Monolina fructicolaspore germination[1]	Phytophthora cinnamomi on lupin[2]	Rhizoctonia solina on cotton[3]	Fusarium oxysporum on tomato[4]
13	++	++	−	+
14	++	++	++	+
17	+	+	−	+
23	−	−	−	++
27	−	+	++	−
36	+	+	+	−
42	++	++	−	−
44	++	++	−	+
46	++	++	+	−
59	−	−	++	−
67	++	+	−	+
78	++	++	+	−

1. 50% inhibition of spore germination of *M. fructicola*

≤ 5 ppm ++
>5≤ 50 ppm +
>50 ppm −

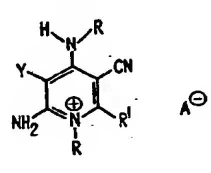
2. Protection of lupin seedlings from infection by *P. cinnamomi*

≤2 ppm ++
>5≤8 ppm +
>8 ppm −

3. Infection of cotton seedlings by *Rh. solani*
100% protection at 16 kg/ha (soil application) ++
50% protection at 16 kg/ha (soil application) +

4. Infection of tomato seedlings by *F. oxysporum*
100% protection at 8 kg/ha (soil application) ++
50% protection at 8 kg/ha (soil application) +

WHAT WE CLAIM IS:—
1. Compounds of the general formula I



I

wherein:
Y is hydrogen or halogen;

R is straight- or branched-chain, substituted or unsubstituted alkyl or allyl; substituted or unsubstituted cycloalkyl; or aralkyl;

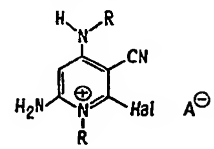
R′ is hydrogen; halogen; sulphonate; azido; a radical of the formula —NH—SO$_2$R$_1$, wherein R$_1$ represents a substituted or unsubstituted aryl group or a straight-or branched-chain, substituted or unsubstituted alkyl group; a radical of the formula

$$—S—\underset{\underset{S}{\|}}{C}—N—$$

-(lower alkyl)$_2$; a radical of the formula —CH(CN)—R$_2$, wherein R$_2$ represents —COOH, —COO(lower alkyl) or —NH—CO——NH$_2$, or a radical of the formula —NH—R″, —S—R″ or —O—R″, wherein R″ represents hydrogen, substituted or unsubstituted, straight-or branched-chain alkyl, alkenyl or alkynyl, substituted or unsubstituted aryl or aralkyl, or cyano; and

A⊖, which is not present when R′ contains an anionic group, represents a halide anion.

2. Compounds of the general formula III



III

wherein

Hal represents halogen; and

R and A⊖ are as defined in claim 1.

3. Compounds of general formula I defined in claim 1, substantially as herein described in any one of the Examples.

4. A process for the preparation of compounds of the general formula I defined in claim 1, which comprises reacting a compound of the general formula II

$$\begin{array}{c} H\quad R \\ \backslash\ / \\ N \\ | \\ CO \\ | \\ CH_2 \\ | \\ CN \end{array}$$

in which R is as defined in claim 1 with a phosphorous halide or oxyhalide to produce a compound of the general formula III defined in claim 2; and, if desired, the compound of general formula III is halogenated in the 3-position and/or the 6-halo substituent is replaced by other radicals represented by R′ as defined in claim 1 in manner known *per se*.

5. A process as claimed in claim 4, wherein the compound of general formula II is dissolved in an organic solvent, the phosphorous halide or oxyhalide is added to the solution and the mixture warmed under reflux.

6. A process for the preparation of compounds of the general formula I, defined in claim 1, substantially as herein described in any one of the Examples.

7. Compounds of the general formula I defined in claim 1, whenever prepared by a process claimed in any one of claims 4 to 6.

8. A method of controlling fungal infection of plants which comprises treating the fungi, the plants, the soil or the seeds of the plants with an effective amount of a compound as claimed in any of claims 1 to 3 or 7.

9. A composition for controlling the growth of fungi which comprises an inert carrier and an effective amount of a compound as claimed in any of claims 1 to 3 or 7.

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